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Crystal structure of potassium succinate trihydrate, $C_4H_4O_4K_2 \cdot 3\,H_2O$

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Abstract. The crystal structure of the title compound has been determined. MW = 248.315, the crystals are orthorhombic, space group *Pnma* with $a = 15.695(9)$, $b = 7.592(3)$, $c = 8.508(3)$ Å, $V = 1013.8(8)$ Å^3, $Z = 4$, $D_c = 1.627(3)$ Mg · m^{-3}, $\mu = 8.550$ mm^{-1}, $\lambda_{CuK\alpha}$, $F(000) = 512$. It was refined to $R = 0.051$, $Rw = 0.054$, for 846 unique observed reflections with $I > 2\,\sigma(I)$. The ion succinate lies on a mirror plane as well as the water molecules. The K^+ ion is linked to six oxygen atoms in a distorted octahedral coordination with distances ranging from 2.716(3) to 3.070(4) Å. The molecules are linked by hydrogen bonds and coupled through potassiums ions forming layers at $^1/_4$ and $^3/_4$ of *b*.

Introduction

In the course of a systematic study of vibrational spectra of alkaline succinates the question of how the introduction of water of crystallization could affect the geometry of the succinate ion has been arisen. A structural study of some alkaline succinates has been carried out to light out the problem. In the present paper, the crystal structure of potassium succinate trihydrate is reported.

Experimental and determination of the structure

Recrystallized from water, a prismatic, colourless, transparent crystal was sealed in a Lindemann glass capillary. Accurate cell parameters were determined by least-squares methods from the setting angles of 28 reflections,

Table 1. Coordinates and thermal parameters with e.s.d.s in parentheses; U_{eq} ($\cdot 10^3$) defined as one third of the trace of the orthogonalized U tensor

	x	y	z	U_{eq}
K	0.1575(6)	0.0071(1)	0.5598(1)	35(1)
O1	0.2344(2)	0.2500	0.3732(5)	40(1)
O2	0.0280(3)	0.2500	0.5356(5)	43(1)
O3	0.3742(2)	0.2500	0.7876(5)	61(2)
O11	0.2213(2)	0.2500	1.0450(4)	33(1)
O12	0.1998(2)	0.2500	0.7875(4)	37(1)
C1	0.1733(2)	0.2500	0.9274(6)	24(2)
C2	0.0774(3)	0.2500	0.9488(7)	33(2)
C3	0.0477(3)	0.2500	1.1170(6)	37(2)
C4	−0.0482(3)	0.2500	1.1420(6)	28(2)
O41	−0.0726(2)	0.2500	1.2827(4)	36(1)
O42	−0.0975(3)	0.2500	1.0282(5)	61(2)
	x	y	z	U
H11	0.2162	0.2500	0.2502	38
H12	0.2900	0.2500	0.3960	38
H21	−0.0200	0.2500	0.6000	45
H22	0.0080	0.2500	0.4300	45
H31	0.3960	0.2500	0.6842	61
H32	0.3100	0.2500	0.8000	61
H2	0.0564	0.1194	0.8972	56
H3	0.0746	0.1439	1.1795	41

$11 < \theta < 45°$, measured on a Philips PW 1100 four-circle computer-controlled diffractometer, graphite monochromated Cu$K\alpha$ radiation. Crystal data are given in the abstract.

Intensities were measured from the same crystal on the same diffractometer for $2 < \theta < 65°$. The $\omega/2\,\theta$ scan mode was used. Two reflections were used as standard and remeasured after every 90 min. They showed no systematic variation. 931 reflections were collected, 846 considered observed with $I > 2\,\sigma(I)$, σ being determined from counting statistics. Lorentz and polarization corrections were applied. No corrections were made for absorption since an estimation of this factor plus ϕ-scan data, showed the effect to be quite small.

The structure was solved by direct methods (MULTAN 1980, Main et al.). The best E map (214 reflections) revealed K^+ and confirmed the position on a mirror plane for the succinic ion; these atoms were used to phase $(F_o - F_c)$ maps to give the positions of the remaining non-hydrogen atoms. Isotropic refinement by full-matrix least-squares reduced R to 0.124 showing anisotropic motion of the atoms. Refinement continued by full-matrix least-squares with anisotropic thermal parameters for the non-

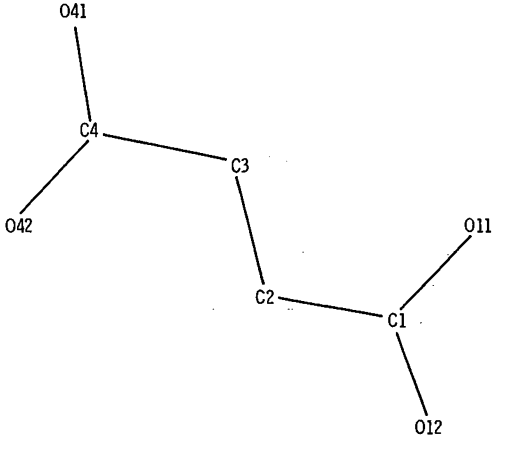
hydrogen atoms; H atoms of the succinate ion were found from succesive difference maps and those of the water molecules were located from geometric calculations (those values are in agreement with areas of positive $\varrho(F_o - F_c)$ values looking for H positions). They were included in the refinement with isotropic thermal parameters of the atoms to which they were attached. An empirical weighting scheme (Martínez-Ripoll and Cano, 1975) gave no trends in the function minimized $\Sigma\omega(|F_o| - |F_c|^2)$. Unit weight was used. The final R values were $R = 0.053$ ($Rw = 0.056$). Average and maximum shift/error ratios were 0.003 and 0.007 respectively. A final difference map revealed a peak of 0.46 $eÅ^{-3}$ near the K atom.

The atomic scattering factors, corrected for anomalous dispersion, were taken from International Tables for X-ray Crystallography (1974). Computations were carried out with programs of the X-Ray System (Stewart, Kundell and Baldwin, 1970), PARST (Nardelli, 1982) and PESOS (Martínez-Ripoll and Cano, 1975) running on the VAX 11/750 computer.

Final atomic coordinates and equivalent values (U_{eq}) of the anisotropic thermal parameters are given in Table 1. Bond angles and bond distances are listed in Table 2[1].

Description and discussion of the structure

The following scheme shows the atomic numbering of the succinate ion.



The bond lengths and angles of the succinic fragment are similar to those found in literature (Sime, 1970; McAdams, 1971; Gupta, 1983) and this fact shows that the introduction of water molecules doesn't provoke any

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51323, the names of the authors and the title of the paper

Table 2. Interatomic distances and angles in the succinate ion (standard deviations in parentheses)

O11–C1	1.252(6) Å	O11–C1–O12	123.8(4)°
O12–C1	1.260(6)	O12–C1–C2	116.1(5)
C1–C2	1.517(7)	O11–C1–C2	120.0(5)
C2–H2	1.133(3)	C1–C2–C3	114.9(5)
C2–C3	1.505(8)	C2–C3–C4	116.1(5)
C3–H3	1.054(4)	C3–C4–O42	120.6(5)
C3–C4	1.519(8)	C3–C4–O41	115.8(5)
C4–O41	1.257(7)	O41–C4–O42	123.5(5)
C4–O42	1.240(7)		

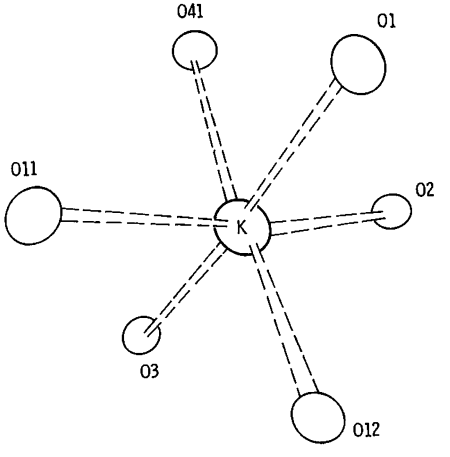


Fig. 1. Coordination around K ion. (See Table 3 and text for interatomic distances and angles)

modification in the geometry of the succinate ion. The average value of the C–O distances is 1.252(5) Å [1.240(6) to 1.260(6) Å] and that of the O–C–O angles 123.6(4)°. It is clear from the present work that the carboxyl group in the title compound is almost symmetric. Compared with that reported by Dunlop (1973) for the super-acid salt potassium trihydrogen di-succinate we find a great difference which is evidenced by the dimensions of the carboxyl groups; here, both groups can be identified as ionized carboxylates.

The succinate ion is plane and is situated in a symmetry plane ($y = \frac{1}{4}$) as well as the water molecules; the succinic groups are connected by hydrogen bondings to the water molecules (O1 and O3) forming a network with weak bonds. The potassium ions, located in general positions, connect through their coordination bonds the succinate ions and the water molecules placed

Table 3. Environment of the potassium ion (standard deviations in parentheses)

a) $K^+ \ldots O$ distances (Å)		b) $O \ldots K^+ \ldots O$ angles (°)			
$K-O1^{(0)}$	2.716(3)	O1–K–O2	80.2(1)	O2–KO3	104.5(1)
$K-O2^{(0)}$	2.753(3)	O1–K–O12	81.3(1)	O12–K–O11	110.1(1)
$K-O12^{(0)}$	2.756(3)	O1–K–O11	98.6(1)	O12–K–O41	104.6(1)
$K-O41^{(I)}$	2.717(3)	O1–K–O41	173.7(1)	O12–K–O3	174.3(1)
$K-O11^{(II)}$	2.728(3)	O1–K–O3	93.6(1)	O11–K–O41	81.4(1)
$K-O3^{(II)}$	3.070(4)	O2–K–O12	77.4(1)	O11–K–O3	67.9(1)
		O2–K–O11	172.2(1)	O41–K–O3	80.6(1)
		O2–K–O41	99.0(1)		

Symmetry code: (0) x, y, z; (I) $\bar{x}, \bar{y}, -z + 2$; (II) $-x + {}^1/_2, y - {}^1/_2, z - {}^1/_2$

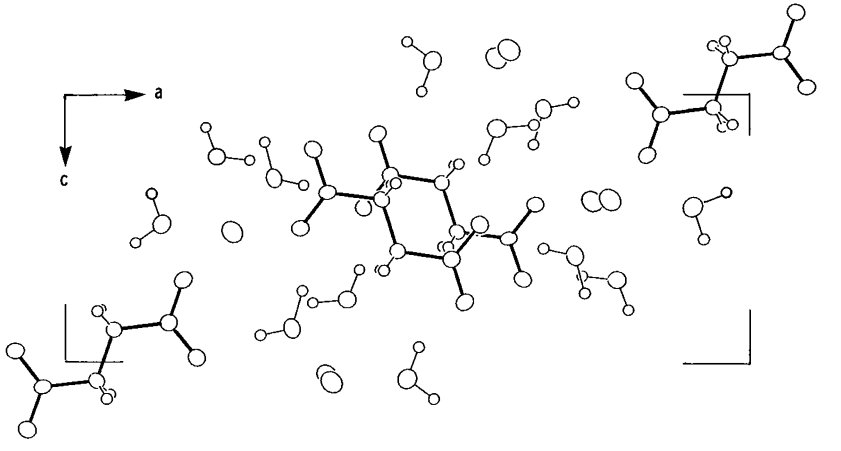


Fig. 2. Packing of the molecule viewed down the *b* axis

on the symmetry planes. The potassium ion presents octahedral coordination, making contact with six oxygen atoms (Fig. 1): three belonging to different succinate units and the remaining three to water molecules, with distances ranging from 2.716(3) to 3.070(4) Å (Table 3). The water molecules, coordinated to the potassium ion form, in turn, hydrogen bondings with the oxygens of the succinate ion, forming layers at ¼ and ¾ from the *b* axis.

A list of bond lengths and angles associated with the water molecules, together with their estimated standard deviations have been deposited.

The packing of the molecules in the unit cell, (010) projection, is shown in Fig. 2.

References

Dunlop, R. S., Speakman, J. C.: The crystal structure of, and the hydrogen bonding in, the super-acid salt potassium tri-hydrogen di-succinate: a direct solution of the phase problem based on neutron-diffraction measurements. Z. Kristallogr. **138**, 100–112 (1973)

Gupta, M. P., Sahu, R. D., Raja Ram, Maulik, R. R.: The crystal structure of manganese(II) succinate tetrahydrate. Z. Kristallogr. **163**, (55–158 (1983)

International Tables for X-ray Crystallography, vol. 4. Birmingham: Kynoch Press 1974

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P., Woolfson, M. M.: MULTAN. System of computer programs for automatic solution of crystal structures from X-ray diffraction data. Univs. of York, England and Louvain, Belgium (1980)

Martínez-Ripoll, M., Cano, F. H.: PESOS. A computer program for the automatic treatment of weighting schemes. Instituto Rocasolano. C.S.I.C. Madrid, Spain (1975)

McAdam, A., Currie, M., Speakman, J. C.: The crystal structures of the acid salts of some dibasic acids. Part. IV. Potassium hydrogen succinate: X-ray and Neutrondiffraction studies. J. Chem. Soc. (A) 1994–1997 (1971)

Nardelli, M. PARST. A computer program. Univ. Parma, Italy (1982)

Sime, J. G., Speakman, J. C., Parthasarathy, R.: The crystal structures of the acid salts of some dibasic acids. Part II. Potassium hydrogen malonate: two X-ray studies. J. Chem. Soc. (A) 1919–1923 (1970)

Stewart, J. M., Kundell, F. A., Baldwin, J. C.: THE X-RAY SYSTEM. Computer Science Center. University of Maryland, USA